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Sorption of aged dicamba residues in soil†

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Abstract: The effect of aging (residence time in soil) on dicamba (3,6-dichloro-2-methoxybenzoic acid) and a major metabolite, 3,6-dichlorosalicylic acid (3,6-DCSA) sorption was determined in an unamended and a carbon-amended sandy loam and in a silt loam soil. During the incubation, sequential solvent extraction with 0.01 M calcium chloride solution and aqueous acetonitrile + hydrochloric acid was used to determine the solution and sorbed concentrations of dicamba and 3,6-DSCA, and sorption coefficients were calculated. Dicamba was weakly sorbed to soil (K_d < 0.7). In contrast to some other classes of pesticides, sorption of dicamba did not significantly increase with aging, at least not until <15% of the applied dicamba remained. 3,6-DSCA was strongly sorbed to soil (K_d > 8) and the $K_{d\text{-}a}$ value increased by a factor of 2–6 during a 28-day aging period. Addition of a carbon source to the soil had minimal effect on the strength of sorption of aged dicamba. However, it did appear to decrease 3,6-DSCA availability to soil micro-organisms; once formed 3,6-DSCA was not further mineralized. While it appears that sorption can be well characterized for weakly sorbed pesticides using the batch equilibration method with freshly treated soils, this procedure may not be adequate for more strongly sorbed pesticides and their degradates.

Keywords: sorption; degradation; dicamba; herbicide

1 INTRODUCTION

The fate of pesticides in the environment is governed by retention, transformation and transport processes, and the interaction of these.[1,2] The capacity of soil to retain or sorb pesticides from aqueous solutions is a key parameter controlling the extent to which pesticides leach through soil into ground water or run off into surface water. While sorption is affected by the physical and chemical properties of the pesticide and soil,[2] it also appears that sorption can be affected by the residence time in the soil.[3] For instance, increases in apparent sorption coefficients, $K_{d\text{-}a}$, with incubation time have been observed for a variety of classes of pesticides such as triazines,[4,5] acetanilides,[3,5] pyridine carboxylic acids,[6] amides,[7] carbofuran,[8] substituted ureas,[7,9–13] nitroguanidines,[14] imidazolinones,[15,16] sulfonylureas[12] and sulfonylaminocarbonyltriazolinones.[17]

The increase in apparent sorption with aging (in some case called desorption hysteresis) has been attributed to a variety of factors,[18] including diffusion of the chemicals to less accessible sorption sites (slow equilibria), and preferential hydrolysis/degradation of solution phase or readily available chemical, leaving more strongly sorbed chemical.[12] It has also been suggested that sorbent deformation may be the universal cause of sorptive hysteresis.[18] It is difficult to distinguish between the possible mechanisms; the net result is probably a combination of them. Regardless of the mechanism of the increase in the apparent sorption, the net effect is that use of simplistic equilibrium partitioning coefficients based on freshly treated samples under slurry conditions will predict much greater movement of these chemicals than if we used the sorption coefficients determined on aged residues. For instance, Pignatello *et al*[19] found that the mobility of freshly added atrazine and metolachlor was greater than for aged residues. If we are to improve models describing pesticide availability for transport and biodegradation in soil, we need to understand better the complex interactions of the sorption–desorption and degradation processes, particularly for aged residues of herbicides that are not appreciably sorbed in freshly treated soils.

Several investigators have reported that dicamba, a weak acid herbicide (pK_a, 1.95),[20] dissipated rapidly from soil with half-lives ranging from days, under favorable conditions, to weeks.[21–24] Metabolism by

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soil micro-organisms would appear to be the major pathway of dicamba degradation under most soil conditions.[21,22,25] Dicamba is completely mineralized or is biologically transformed to other compounds, including 3,6-dichlorosalicylic acid (3,6-DCSA) (pK_a, 1.95)[20] by demethylation and this, in turn, can be hydroxylated to give 2,5-dihydroxy-3,6-dichlorobenzoic acid (2,5-diOH) metabolite,[21] both of which may become reversibly or irreversibly bound to soil, competing with dicamba for possible sorption sites.[21,26]

In spite of rapid dissipation, dicamba would be considered highly mobile in soils[24,26,27] based on low sorption, with K_d values ranging from 0 to 0.3.[20,28–30] As a result of runoff, dicamba has been found in farm ponds[31] and rivers.[32,33] Dicamba also readily leaches and has been found in tile drains[34] and in pan lysimeters >1.2 m below the soil surface,[35,36] in part as the result of preferential flow.[37] Dicamba itself has been shown to leach to a greater extent than the primary degradate, 3,6-DCSA.[38]

The primary objective of this research was to determine the effect of aging on sorption of dicamba and metabolites in soil. Sorption of dicamba and 3,6-DCSA to soil was determined as a function of time. Whether an added carbon source could affect sorption, particularly in the case of 3,6-DCSA, a phenolic acid, was also investigated. A variety of phenolic compounds, including degradation intermediates of pesticides, have been shown to bind to soil organic matter by oxidative coupling or polymerization reactions.

2 MATERIAL AND METHODS

2.1 Chemicals and soils

Dicamba (99% purity) was obtained from Chem Service (West Chester, PA), 3,6-dichlorosalicylic acid (3,6-DCSA; 99% purity) from Sandoz Crop Protection Corporation (Des Plaines, IL) and 2,5 dihydroxy-3,6-dichlorobenzoic acid (2,5-diOH; 99% purity) from Chem Service. Uniformly ring-labeled ^{14}C-dicamba (106 MBq mmol^{-1}, radiochemical purity >99%) was purchased from Pathfinder laboratories (St Louis, MO).

Soil samples of Kim loam, Port Byron silt loam, Webster clay loam and Estherville sandy loam were collected from three depths. Each soil was sieved through a 5-mm screen, thoroughly mixed, and stored in sealed plastic bags at room temperature. Fresh Verndale sandy loam and Waukegan silt loam soils were passed through a sieve (<2 mm) and stored at 4 °C until used. Soil texture was determined by the hydrometer method. Soil pH was measured in 2:1 (w/w) soil:deionized water. Organic carbon (OC; % m/m) content of the soil was determined by dichromate oxidation. Finely ground wood from Loblolly pine (*Pinus taeda* L), which contained 30% lignin, was dried and passed through a sieve (<1 mm). Selected physical and chemical properties of the soils are listed in Table 1.

2.2 Batch sorption studies

The batch equilibration method with 1:1 soil:dicamba solution (w/w) in 0.01 M calcium chloride was used in the sorption studies. Four initial dicamba concentrations were 0.45, 1.36, 4.52 and 13.67 μM, spiked with 33 Bq ml^{-1} ^{14}C-dicamba. The sorption studies were conducted using duplicate samples of Kim loam, Port Byron silt loam, Webster clay loam and Estherville sandy loam soils. A 10-ml aliquot of each solution was added to 10 g of air-dried soil in a 25-ml glass centrifuge tube and sealed with a Teflon-lined cap. At the end of 24-h equilibration (shaking horizontally) at 22 (±2) °C, an automated robotic system was used to process the samples.[39] In brief, the automated steps were: agitate using a vortex mixer for 20 s; centrifuge for 20 min at 1371 *g*; transfer 4 ml of the supernatant into a 20-ml scintillation vial. Preliminary studies showed that sorption equilibrium was attained in less than 24 h.

The desorption study was conducted using the same robotic system as in the sorption study, and

Table 1. Characterization of soils

Soil	Taxonomy, location	Soil depth (cm)	OC (%)	Clay (%)	Sand (%)	pH
Estherville sandy loam	Typic Hapludoll, MN	0–13	4.2	21	46	6.0
		25–36	1.9	20	52	6.7
		46–56	0.9	15	61	6.9
Port Byron silt loam	Typic Hapludoll, MN	0–15	2.3	24	9	6.8
		30–45	1.3	26	6	6.4
		60–75	0.5	25	11	7.3
Webster clay loam	Typic Hapludoll, MN	0–15	4.0	33	29	5.6
		30–45	1.0	39	21	6.7
		60–75	0.3	27	42	7.4
Kim loam	Ustic Torriorthent, CO	0–15	1.7	35	21	7.9
		30–45	1.1	39	13	8.3
		60–75	1.4	34	17	8.4
Waukegan silt loam	Typic Hapludoll, MN	0–15	2.6	23	17	5.8
Verndale sandy loam	Udic Argioroll, MN	0–15	1.4	28	51	6.1

4 ml of fresh 0.01 M calcium chloride was added to the tubes to replace the 4 ml of supernatant previously withdrawn. Desorption studies with five sequential cycles were conducted on the samples with the initial concentration of 4.52 μM. The samples were agitated for 2 min using a vortex mixer to resuspend the soil pellet. The samples were then taken off the robotic system and equilibrated for 24 h for the next desorption cycle. The radioactivity in the supernatant was determined by liquid scintillation spectroscopy (LSS).

Dicamba sorption isotherms were calculated using the Freundlich equation:

$$\log x/m = \log K_f + (1/n) \log C$$

where x/m ($\mu mol\,kg^{-1}$) is dicamba sorbed by soil; C ($\mu mol\,litre^{-1}$) is the dicamba content of the supernatant solution after equilibration; K_f and $1/n$ are empirical constants calculated from the above equation; $\log K_f$ is the y intercept when C equals 1 and $1/n$ is the slope of the equation. The units of K_f are $\mu mol^{(1-1/n)}$ $litre^{1/n}$ kg^{-1}. Calculations were based on the assumption that no degradation of dicamba occurred during sorption studies; preliminary studies showed that there was no degradation in these four soils during the 5 days during which the experiments were run. The lack of degradation was presumed to be due to a lag phase prior to start of degradation as the result of air-dry storage of these soils. The amount of dicamba sorbed by the soil was assumed to be the difference between the dicamba in the initial and final solution as calculated from dpm measurement and the specific activity of ^{14}C-dicamba. The amount of sorbed dicamba for each desorption cycle was calculated from the difference between dpm values for the initial solution and the desorption solution minus the amount in the 4-ml taken out for counting of the previous sorption/desorption cycle. Statistical analysis of the sorption studies included tests for homogeneity of variance, comparison of slopes and elevations of the regression lines, and calculation of the standard deviation of the y intercept ($\log K_f$) and slope ($1/n$).

2.3 Aged chemical sorption study

Triplicate fresh Verndale sandy loam and Waukegan silt loam soil samples (20 g) in glass centrifuge tubes (50 ml) were each spiked with ^{14}C-dicamba solution (240 μl). The resultant concentration of 0.25 $mg\,kg^{-1}$ corresponds to a typical field application rate of 0.28 $kg\,ha^{-1}$, assuming uniform incorporation to a depth of 7.5 cm. For the amended treatment, 0.4 g of wood was added to the soil and mixed thoroughly. Ammonium nitrate solution was added to the wood-amended soil in order to make the C/N ratio in the amended soil the same as in the unamended soil, and the water content was adjusted for all samples to a matric potential of −33 kPa, both of which are particularly important in maintaining comparable environments for microbial activity in carbon-amended and unamended soils.[40] For instance, water contents at −33 KPa were 0.12 and 0.10 $g\,g^{-1}$ for the amended and unamended soil, respectively.

Each centrifuge tube was placed in a 500-ml Nalgene plastic bottle along with a glass vial containing sodium hydroxide solution (1 M; 5 ml). The bottle was tightly sealed. The amended and unamended soils were incubated at 28 °C for up to 28 days; samples were analyzed at seven times (0, 1, 3, 7, 10, 14, 28 days).

^{14}C-Carbon dioxide resulting from the mineralization of the ring-labeled ^{14}C-dicamba and total carbon dioxide resulting from microbial respiration was trapped in the sodium hydroxide. On every sampling date the sodium hydroxide solution was analyzed for ^{14}C-carbon dioxide and total carbon dioxide. The radioactivity in duplicate aliquots of the sodium hydroxide solution (1 ml), mixed with Ecolite scintillation cocktail (10 ml), was determined by liquid scintillation counting (LSC) using a Model 1500 Tri-Carb liquid scintillation analyzer (Packard Instruments Co, Downers Grove, IL). Total carbon dioxide was determined using a Dohrman Carbon Analyzer.

At each sampling time, dicamba and metabolites were first extracted from soils by adding calcium chloride solution (0.01 M; 20 ml) to the centrifuge tube containing the soil and shaking the tubes on a reciprocating shaker for 24 h. After centrifugation (2988 g for 30 min), the clear supernatant was transferred to a glass test tube. Dicamba and metabolites were then extracted from the soil by adding acetonitrile + water + glacial acetic acid (70 + 27 + 3 by volume; 30 ml) to the previously extracted soil and shaking for 24 h. After centrifugation (2988 g for 30 min), the clear supernatant was transferred to a glass test tube. The remaining dicamba and metabolites in the soil were then extracted by transferring the solvent-extracted soil into a 250-ml Erlenmeyer flask with hydrochloric acid (1 M; 50 ml) and heating under reflux for 4 h. Preliminary experiments showed the stability of dicamba after a 4-h reflux with 1 M hydrochloric acid. After cooling, the mixture was filtered through a cellulose filter. Residual soil was washed with distilled water and the hydrochloric acid supernatant volume was made up to 100 ml. The final extracted soil was air dried under a hood.

The total radioactivity in each extract was determined by liquid scintillation counting (LSC) after mixing an aliquot (1 ml) of the extract with Ecolite scintillation cocktail (6 ml). Counts per minute were converted to disintegrations per min (dpm) using the external standard ratio method to correct for quenching. The percentage of ^{14}C-dicamba residues extractable by each extraction method was calculated from the ratio of the dpm extractable to the total dpm spiked in each sample.

Triplicate subsamples (0.3 g) were taken from the final air-dried, extracted soil and mixed with an

equal volume of microcrystalline cellulose powder. The samples were oxidized for 1.4 min using a Model 306 sample oxidizer (Packard Instruments, Downers Grove, IL). ^{14}C-Carbon dioxide evolved during combustion was trapped in Carbosorb solvent (Packard Instruments, Downers Grove, IL), then mixed with Permafluor (Packard Instruments, Downers Grove, IL) in a liquid scintillation vial, and quantified by LSC.

For liquid–liquid partitioning of dicamba and metabolites from the aqueous fractions of the extraction solvents, the volume of calcium chloride extracts was first increased to 50 ml with 1 M hydrochloric acid. Acetonitrile was evaporated from the aqueous acetonitrile extracts and the remaining aqueous phase increased to 50 ml with 1 M hydrochloric acid. Solutions were extracted with dichloromethane (4 × 10 ml). In each case, the combined dichloromethane extracts were evaporated at 35 °C under reduced pressure just to dryness, redissolved in acetonitrile (1 ml) and stored at −18 °C until analyzed for ^{14}C-dicamba and metabolites. The amount of ^{14}C polar residues remaining in the aqueous phase was determined by LSC.

Samples were analyzed using a Model HP1090 high performance liquid chromatograph (Hewlett Packard, Avondale, PA) with a Supelcosil ABZ + column (2.1 mm × 25 cm, 5 μm) (Supelco, Inc, Bellefonte, PA) equilibrated at 50 °C, utilizing a mobile phase obtained from a gradient of two solutions: KH_2PO_4 (0.025 M; pH = 2.35) and acetonitrile, at a flow rate of 0.75 ml min^{-1}, starting at 50% of acetonitrile and finishing at 80% of acetonitrile. Detection of dicamba, 3,6-DCSA and 2,5-diOH was carried out at 205 nm and compared with high purity standards. Samples were then collected as different fractions in different vials dictated by retention time of standards and ^{14}C determined by LSC.

To calculate sorption coefficients, $K_{d\text{-}a}$, as a function of incubation time, the amounts of parent dicamba and 3,6-DCSA degradate recovered in calcium chloride solution, aqueous acetonitrile and hydrochloric acid from the incubated Verndale sandy loam and Waukegan silt loam soils were determined. The aqueous acetonitrile/hydrochloric acid extractable corresponded to the sorbed concentration in the batch method, and the calcium chloride extractable corresponded to the solution concentration; $K_{d\text{-}a}$ = amount dicamba or 3,6-DCSA extractable by acetonitrile/hydrochloric acid (μmol g^{-1})/amount dicamba or 3,6-DCSA extractable by calcium chloride (μmol ml^{-1}).

3 RESULTS AND DISCUSSION

3.1 Laboratory sorption studies

The Freundlich equation adequately described the sorption of dicamba for the four soils. Sorption of dicamba was minimally concentration-dependent, as indicated by 1/*n* values (mean 0.87; Table 2). The magnitude of the K_f values (0.004–0.50) indicated that dicamba is weakly sorbed to the four soils. The $K_{f,oc}$($K_{f,oc} = K_f \times 100/OC$) values for the four soils ranged from 0.4 to 40. Low adsorption of dicamba to soils has been observed previously.[20,28,29] The small amounts of dicamba that were sorbed did not readily desorb from soil. Desorption of dicamba from soils from different soil depths was hysteretic as indicated by the sorption 1/*n* >> desorption 1/*n* values (Table 2). In contrast, Murray and Hall[20] demonstrated that dicamba readily desorbed from soils.

There was no correlation of measured soil properties as a function of soil depth and dicamba sorption–desorption. Regardless of the soil properties, only a small fraction of dicamba was sorbed to soil, leaving most of the compound in solution and available for leaching and microbial degradation. Because sorption was minimally concentration dependent, we could use a single concentration to determine the effect of aging on dicamba sorption to soil.

3.2 Aged sorption studies

3.2.1 ^{14}C distribution

Total recovery of ^{14}C distributed between calcium chloride, acetonitrile and hydrochloric acid extracts,

Table 2. Freundlich sorption parameters of dicamba as a function of soil types and depth

Soil type	Depth (cm)	K_f ($\mu mol^{(1-1/n)} litre^{(1/n)} kg^{-1}$)	$K_{f,oc}$	1/*n* Sorption	1/*n* Desorption
Kim	0–15	0.04 (0.02–0.07)[a]	2.4 (1.2–4.1)	0.85 (±0.15)	0.0
	30–45	0.004 (0.002–0.008)	0.4 (0.2–0.7)	0.76 (±0.47)	0.0
	60–75	0.08 (0.06–0.12)	5.7 (4.3–8.6)	0.88 (±0.09)	0.12 (±0.04)
Port Byron	0–15	0.25 (0.23–0.28)	10.9 (10.0–12.2)	0.91 (±0.03)	0.05 (±0.03)
	30–45	0.24 (0.20–0.28)	18.5 (15.4–21.5)	0.86 (±0.04)	0.22 (±0.05)
	60–75	0.11 (0.08–0.18)	22.0 (16.0–36.0)	1.04 (±0.11)	0.24 (±0.06)
Webster	0–15	0.50 (0.47–0.53)	12.5 (11.8–13.3)	0.82 (±0.01)	0.0
	30–45	0.15 (0.14–0.17)	15.0 (14.0–17.0)	0.82 (±0.03)	0.19 (±0.02)
	60–75	0.12 (0.11–0.14)	40.0 (36.7–46.7)	0.86 (±0.03)	0.05 (±0.02)
Estherville	0–13	0.35 (0.33–0.38)	8.3 (7.9–9.1)	0.88 (±0.02)	0.41 (±0.04)
	25–36	0.13 (0.11–0.16)	6.8 (5.8–8.4)	0.92 (±0.05)	0.13 (±0.04)
	46–56	0.03 (0.01–0.07)	3.3 (1.1–7.9)	1.32 (±0.22)	0.0

[a] Numbers in parenthesis are standard deviation of the means.

mineralized carbon dioxide and bound residues was 88.7 (±12.1)% for unamended and 91.7 (±8.7)% for carbon-amended sandy loam soil, and 84.1 (±11.0)% for unamended and 86.2 (±7.3)% for amended silt loam soil, over all sampling times. Considering the number of steps involved in the extraction and analyses, the ^{14}C mass balance was excellent.

In unamended sandy loam soil, there was a rapid decrease in total extractable ^{14}C [Σ(calcium chloride + acetonitrile + hydrochloric acid fractions)]. The initial decrease of total extractable ^{14}C was due to the formation of bound residues, which constituted 22% of applied ^{14}C after 3 days (Fig 1). Beyond 3 days, the amount of bound residues remained relatively constant and was 26% of applied ^{14}C at 28 days. The rest of the decrease in extractable ^{14}C was due to the continuous mineralization of dicamba. While there was very little ^{14}C-carbon dioxide evolved during the first 3 days, 30% of the ^{14}C was mineralized at 28 days. The same pattern was observed in the carbon-amended sandy loam soil, except that there was less ^{14}C mineralization (only 10% after 28 days) (Fig 2) than in unamended soil.

Similar results were observed in the unamended silt loam soil (Fig 3). The initial rapid decrease in total extractable ^{14}C was due to the formation of bound residues, 16% of applied ^{14}C after 3 days and 36% after 28 days, and mineralization, 16% of the ^{14}C being mineralized at 28 days. The same pattern was observed in the carbon-amended silt loam soil, except that there was less ^{14}C mineralization (only 6% after 28 days) (Fig 4) than in the unamended soil.

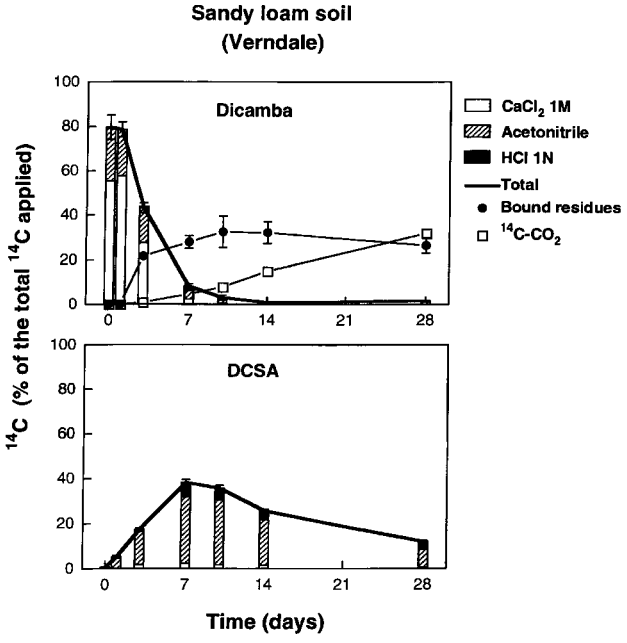

Figure 1. Distribution of ^{14}C-dicamba and ^{14}C-DCSA between extraction solvents, mineralized ^{14}C-carbon dioxide and bound residues as a function of time in unamended sandy loam soil. Standard errors of the measurements are shown when larger than the symbol size.

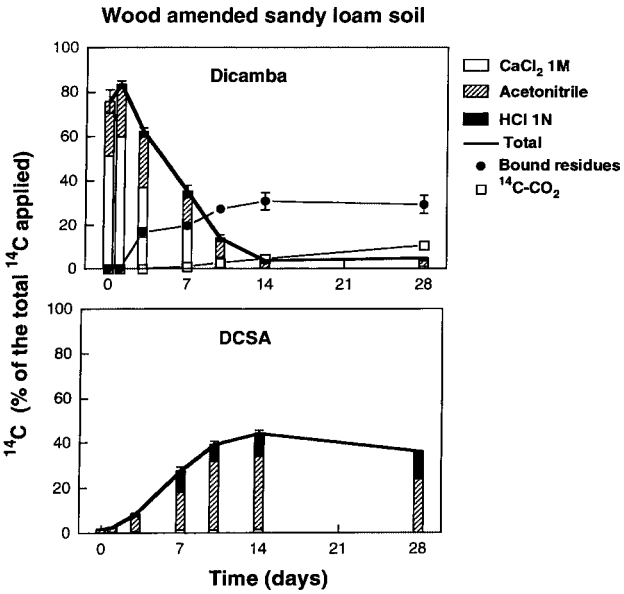

Figure 2. Distribution of ^{14}C-dicamba and ^{14}C-DCSA between extraction solvents, mineralized ^{14}C-carbon dioxide and bound residues as a function of time in carbon amended sandy loam soil. Standard errors of the measurements are shown when larger than the symbol size.

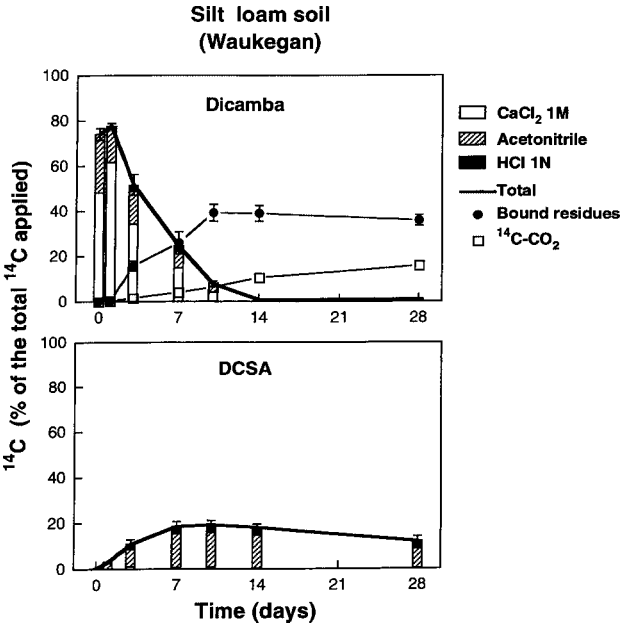

Figure 3. Distribution of ^{14}C-dicamba and ^{14}C-DCSA between extraction solvents, mineralized ^{14}C-carbon dioxide and bound residues as a function of time in unamended silt loam soil. Standard errors of the measurements are shown when larger than the symbol size.

3.2.2 Sorption in aged soil

The sorption coefficient K_d is defined as the ratio of the amount of pesticide sorbed to the amount of pesticide in solution after equilibration. These coefficients have been traditionally determined using the batch equilibration technique as described earlier, where sorbed amounts are not determined directly but calculated from amounts of pesticide lost from solution. In contrast, for calculation of apparent

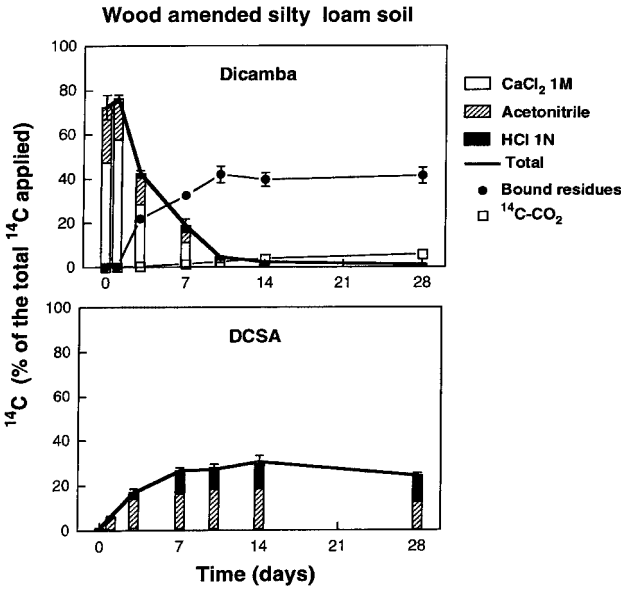

Figure 4. Distribution of ^{14}C-dicamba and ^{14}C-DCSA between extraction solvents, mineralized ^{14}C-carbon dioxide, and bound residues as a function of time in carbon amended silt loam soil. Standard errors of the measurements are shown when larger than the symbol size.

sorption coefficients, $K_{d\text{-}a}$, in this aged residue study, amounts of dicamba and 3,6-DCSA extracted by 0.01 M calcium chloride were equivalent to solution concentrations in the batch equilibration method and amounts of dicamba or DCSA extractable by acetonitrile/hydrochloric acid are equivalent to the amounts of chemicals sorbed to soil. Determination of the amounts of ^{14}C-dicamba and ^{14}C-DCSA in the extracted ^{14}C at each time point resulted in the solution and sorbed concentrations of each chemical, which in turn were used in the calculation of an apparent sorption coefficient, $K_{d\text{-}a}$.

3.2.2.1 *Dicamba.* In unamended sandy loam soil, dicamba concentration decreased rapidly during the incubation, and it was 99% degraded by the end of the incubation (28 days) (Fig 1). More than 80% of the dicamba applied to the soil was degraded within 7 days. Smith and Cullimore[41] similarly found that 80% of applied dicamba degraded within 7 days on a different sandy loam soil. As was previously found,[21] the degradation of dicamba could be described by first-order kinetics; the calculated half-life was 3 days. This is close to the smallest value in the range in half-lives reported for dicamba (4–555 days).[42] $K_{d\text{-}a}$ values were low (<0.6 ml g^{-1}) during the first 3–7 days of incubation when >15% of applied dicamba remained (Table 3). In unamended silt loam soil, results were similar to those in sandy loam soil, dicamba half-life was <6 days. At incubation times when >15% of the applied dicamba was remaining (<7 days after application), sorption was also low, $K_{d\text{-}a} < 0.7$ ml g^{-1}.

In both soils, calculated sorption coefficients only increased with incubation time when <15% of applied dicamba remained. At this point, it appears that during the incubation, the readily available dicamba (0.01 M calcium chloride extractable) degraded faster than the less labile, sorbed chemical (acetonitrile/hydrochloric acid extractable), resulting in higher sorption coefficients. This is in contrast to results for other classes of pesticide, which showed increased sorption with increased aging times.

Carbon amendment had no significant effect on dicamba degradation or sorption. Dicamba degraded rapidly in carbon amended sandy loam soil (Fig 2); the calculated half-life was slightly longer (5 days) than in unamended soil. In 10 days, >80% of dicamba was degraded. However, the majority of the dicamba was readily available (calcium chloride extractable) during the first 3 days, resulting in $K_{d\text{-}a}$ values <0.7 ml g^{-1} (Table 3), similar to those in unamended soil (Table 1). In carbon amended silt loam soil, results were similar to those in unamended soils; dicamba half-life was <6 days. At incubation times when >15% of the applied dicamba was remaining (<7 days after application), sorption was also low, $K_{d\text{-}a} < 0.7$ ml g^{-1}. The lack of effect of added carbon on dicamba sorption agrees with the lack of correlation of sorption with organic carbon content observed in the batch equilibration study.

3.2.3.2 *3,6-DCSA.* As dicamba decreased in unamended soils, the amount of the main metabolic product of dicamba, 3,6-DCSA, increased up to days 7–10 and then decreased (Fig 1) in sandy loam soil, whereas in silt loam soil it increased up to day 7 and then remained the same (Fig 3). Another phenolic metabolite, 2,5-diOH, was observed in small quantities (<1%, data not shown). This metabolite may have been formed in larger quantities, but then rapidly metabolized.[18] 3,6-DCSA was much more strongly bound to soil than dicamba. Aqueous acetonitrile and hydrochloric acid were necessary to extract the majority of the 3,6-DCSA from the soil; only a small amount was in the total calcium chloride extracts. Smith[22] previously found that 3,6-DCSA could not be quantitatively recovered from soil by shaking with calcium chloride solution. This metabolite was shown previously to be more highly sorbed than dicamba.[20,26] Calculated apparent $K_{d\text{-}a}$ values for 3,6-DCSA in the two soils were >8 ml g^{-1} from day 3–28 sampling times (Table 3) when 3,6-DSCA was >15% of applied ^{14}C (Figs 1 and 3). At each sampling date, sorption of 3,6-DCSA on unamended silt loam soil was greater than on the corresponding sandy loam soil from days 3–28 during the incubation (Table 3). Apparent $K_{d\text{-}a}$ values increased by factors of 2 and 6 from days 3 to 28 of the incubation for the sandy loam and silt loam sols, respectively.

Added carbon did not significantly affect the strength of sorption of aged 3,6-DCSA residues. In carbon-amended sandy loam soil, 3,6-DCSA was strongly sorbed, $K_{d\text{-}a} > 9$ ml g^{-1} (Table 3) and the sorption also increased a factor of >2 with aging from days 3–28 (Table 3), when 3,6-DSCA was >15%

Table 3. Dicamba and 3,6-DCSA apparent sorption coefficients ($K_{d\text{-}a}$) calculated from calcium chloride and acetonitrile/hydrochloric acid extractable chemicals in unamended and amended sandy loam and silt loam soils during a 28-day incubation

			Sorption coefficient, K_d (ml g^{-1}) for time of incubation (days)						
Chemical	Soil	Treatment	0	1	3	7	10	14	28
Dicamba	Sandy loam	Unamended	0.43	0.36	0.57	2.04	3.00	4.00	∞[a]
		Amended	0.48	0.39	0.62	0.76	1.46	11.0	2.27
	Silt loam	Unamended	0.54	0.26	0.51	0.66	0.58	∞	∞
		Amended	0.53	0.32	0.51	0.68	1.25	∞	∞
3,6-DCSA	Sandy loam	Unamended	—[b]	—	8.15	12.8	17.0	14.4	16.0
		Amended	—	—	9.28	14.0	25.0	25.0	∞
	Silt loam	Unamended	—	—	9.81	30.0	26.6	59.3	59.0
		Amended	—	—	13.0	22.1	25.0	29.3	60.5

[a] Only sorbed chemical was found, there was no calcium chloride extractable chemical.
[b] Too little 3,6-DCSA was in the soil to accurately calculate apparent $K_{d\text{-}a}$ values.

of the applied ^{14}C remaining (Fig 2). Sorption on amended silt loam soil was similar to that for amended sandy loam, $K_{d\text{-}a}$ was >13 ml g^{-1} and increased by a factor or 4.6 from days 3–28 of the incubation.

In contrast to results in unamended sandy loam and silt loam soils, concentrations of 3,6-DCSA in carbon-amended soils did not decrease from the maximum concentrations observed (Figs 2 and 4). At the end of the incubation, significantly greater amounts of 3,6-DCSA were still in amended soils than in unamended soils, presumably the result of greater sorption to wood residues and decreased availability to soil micro-organisms. The differences in amounts of 3,6-DCSA between amended and unamended soils corresponded to the differences in mineralization of 3,6-DCSA, as evidenced by differences in ^{14}C-carbon dioxide evolution, which was slower in amended soils than in unamended soils.

In contrast to the observed effect of added organic carbon on sorption, Murray and Hall[20] found no significant correlation between 3,6-DCSA sorption and soil organic carbon. They suggested that a build-up of surface organic in no-till systems would not be expected to contribute significantly to sorption of this compound. However, more work is needed in this area. At the end of the 28-day incubation, 11% of the added wood carbon was mineralized (data not shown). Wood carbon mineralization was estimated from the difference in carbon dioxide evolved from soils incubated with and without wood.[43] The mineralization of wood corresponded to the more easily degradable carbon, ie monosaccharides and hemicellulose, but cellulose and lignin were not decomposed. The decomposing wood may have then provided additional strong binding sites for the 3,6-DCSA. A variety of phenolic compounds, including degradation intermediates of pesticides, have been shown to bind to soil organic matter by oxidative coupling or polymerization reactions.[44]

4 CONCLUSIONS

Dicamba was weakly sorbed to soil. In contrast with some other classes of pesticide, sorption of dicamba did not significantly increase with aging, at least not until <15% of the applied dicamba remained. This lack of increased sorption may be the result of a rapid rate of degradation, there was not enough time for diffusion to more strongly sorbing sites. It may also be due to the limited number of sites that have a strong affinity for dicamba. As dicamba degrades, the contribution of the strongly sorbing sites to the calculated apparent $K_{d\text{-}a}$ value is small until only small amounts of dicamba remain. In contrast to dicamba, sorption of the strongly sorbed 3,6-DSCA increased with aging. Addition of a further carbon source to soil had minimal effect on strength of sorption of aged dicamba. However, it did appear to decrease 3,6-DSCA availability to soil micro-organisms; once formed it was not further mineralized. While it appears that sorption can be well characterized for weakly sorbed pesticides using the batch equilibration method with freshly treated soils, it may not be adequate for more strongly sorbed pesticides and their degradates.

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